

ZEOLITE Y ALKYLATION CATALYSTS

FIELD OF THE INVENTION

The present invention is directed to a zeolite Y catalyst having a controlled macropore structure. The present invention is also directed to a catalyst composite comprising zeolite Y and a process for preparing the catalyst composite. The present invention is also directed to alkylation of aromatic hydrocarbons using the catalysts and the catalyst composites of this invention, and the sulfonation and carbonation of the alkylated aromatic hydrocarbons. The catalysts and the catalyst composites exhibit reduced deactivation rates during the alkylation process, thereby increasing the life of the catalyst.

BACKGROUND OF THE INVENTION

It is well known to catalyze the alkylation of aromatics with a variety of Lewis or Bronsted acid catalysts. Typical commercial catalysts include phosphoric acid/kieselguhr, aluminum halides, boron trifluoride, antimony chloride, stannic chloride, zinc chloride, onium poly(hydrogen fluoride), and hydrogen fluoride. Alkylation with lower molecular weight olefins, such as propylene, can be carried out in the liquid or vapor phase. For alkylations with higher olefins, such as C₁₆ olefins, the alkylations are done in the liquid phase, usually in the presence of hydrogen fluoride. Alkylation of benzene with higher olefins is especially difficult, and requires hydrogen fluoride treatment. However, hydrogen fluoride is not environmentally attractive.

The use of the above listed acids is extremely corrosive, thus requiring special handling and equipment. Also, the use of these acids might involve environmental problems. Another problem is that the use of these acids can give less than desirable control on the precise chemical composition of the product produced. Thus, it would be preferable to use a safer, simpler

1 catalyst, preferably in solid state. This simpler process would result in less
2 capital investment, which would result in a less expensive product.

3 Solid crystalline aluminosilicate zeolite catalysts have been known to be
4 effective for the alkylation of aromatics with olefins. Zeolitic materials which
5 are useful as catalysts are usually inorganic crystalline materials that possess
6 uniform pores with diameters in the micropore range that is less than
7 20 angstroms. Zeolites occur naturally and may also be prepared
8 synthetically. Synthetic zeolites include, for example, zeolites A, X, Y, L and
9 omega. It is also possible to generate metaloaluminophosphates and
10 metalosilicophosphates. Other materials, such as boron, gallium, iron or
11 germanium, may also be used to replace the aluminum or silicon in the
12 framework structure.

13 These zeolite catalyst materials are commercially available as fine crystalline
14 powders for further modification to enhance their catalytic properties for
15 particular applications. Processes for the further modification to enhance
16 catalytic properties of the crystalline zeolite catalysts are well known in the art,
17 such as forming the zeolite catalysts into shaped particles, exchanging the
18 cations in the catalyst matrix, etc.

19 Forming the zeolite powders into shaped particles may be accomplished by
20 forming a gel or paste of the catalyst powder with the addition of a suitable
21 binder material such as a clay, an inorganic compound, or an organic
22 compound and then extruding the gel or paste into the desired form. Zeolite
23 powders may also be formed into particles without the use of a binder.
24 Typical catalyst particles include extrudates whose cross sections are circular
25 or embrace a plurality of arcuate lobes extending outwardly from the central
26 portion of the catalyst particles.

27 One problem with catalyst particles used in fixed bed reactors is catalyst
28 deactivation. In most hydrocarbon conversion processes, including alkylation,

1 the primary catalyst deactivation is caused by coke formation. This catalyst
2 deactivation is a serious problem in the use of zeolite catalysts for alkylation
3 reactions. This deactivation problem is well known in the art and it is well
4 understood that the deactivation mechanism can involve polymerization of the
5 olefin into large molecular species that cannot diffuse out of the pores
6 containing the active sites in the zeolitic material.

7 The use of zeolite catalysts for preparation of alkyl aromatics is typically
8 conducted by the catalytic alkylation of aromatic hydrocarbons with normal
9 alpha olefins or branched-chain olefins, and optionally a promotor. The
10 alkylated aromatic hydrocarbons can be converted into corresponding sulfonic
11 acids which can be further converted into alkylated aromatic sulfonates.

12 A number of patents have discussed processes for the preparation of zeolite
13 catalysts and the further shaping and forming of the catalyst particles and
14 extrudates with and without the use of binders. There are also a number of
15 patents disclosing the use of zeolite catalysts for alkylation of aromatic
16 hydrocarbons.

17 U.S. Pat. No. 3,094,383 discloses the preparation of synthetic zeolite
18 materials which upon hydration yield a sorbent of controlled effective pore
19 diameter and in which the sorbent and its zeolite precursor are provided
20 directly in the form of an aggregate.

21 U.S. Pat. No. 3,130,007 discloses the method of preparing sodium zeolite Y
22 with silica to alumina ratios ranging from greater than 3 to about 3.9.

23 U.S. Pat. No. 3,119,660 discloses a process for making massive bodies or
24 shapes of crystalline zeolites. The patent also discloses methods for the
25 identification of the catalyst materials using X-ray powder diffraction patterns
26 in conjunction with chemical analyses.

1 U.S. Pat. No. 3,288,716 discloses that the high "heavy content" of the
2 alkylated aromatic product can be controlled during the alkylation step and
3 has advantages over distilling the alkylated aromatic product to obtain the
4 desired molecular weight.

5 U.S. Pat. Nos. 3,641,177 and 3,929,672 disclose the technique to remove
6 sodium or other alkali metal ions from zeolite catalysts. The '177 patent also
7 discloses that such removal of the sodium or other alkali metal ions activates
8 the zeolite catalysts for the alkylation of aromatic hydrocarbons with olefins by
9 liquid phase reaction.

10 U.S. Pat. Nos. 3,764,533; 4,259,193 and 5,112,506 disclose the "heavy
11 alkylate" content influences neutral sulfonates and overbased sulfonates. In
12 U.S. Pat. No. 5,112,506, the effect of molecular weight distribution or "heavy
13 alkylate" is shown to influence the performance of both Neutral and HOB
14 sulfonates and the di-alkylate content is shown to influence the rust
15 performance of the corresponding sulfonate in U.S. Pat. No. 3,764,533. In
16 U.S. Pat. No. 4,259,193, a mono-alkylate sulfonate is preferred. U.S. Pat.
17 Nos. 3,288,716; 3,764,533; 4,259,193 and 5,112,506 are hereby incorporated
18 by reference for all purposes.

19 U.S. Pat. No. 3,777,006 discloses the use of nucleating centers for the
20 crystallization of crystalline aluminosilicate zeolites having a size in excess of
21 200 microns and characterized by high strength and excellent adsorptive
22 properties.

23 U.S. Pat. No. 4,185,040 discloses the preparation of highly stable and active
24 catalysts for the alkylation of aromatic hydrocarbons with C₂-C₄ olefins. The
25 catalysts are acidic crystalline aluminosilicate zeolites which exhibit much
26 improved deactivation rates.

1 U.S. Pat. No. 4,395,372 discloses an alkylation process for alkylating benzene
2 comprising contacting benzene and lower olefins with a rare earth exchanged
3 X or Y zeolite catalyst in the presence of sulfur dioxide.

4 U.S. Pat. No. 4,570,027 discloses the use of a low crystallinity, partially
5 collapsed zeolite catalyst for producing alkylaromatic hydrocarbons. The
6 alkylation reaction also involves conditioning the catalyst bed with hydrogen
7 prior to conducting the alkylation reaction.

8 U.S. Pat. Nos. 4,762,813; 4,767,734; 4,879,019 and 5,111,792 disclose the
9 preparation of a hydrocarbon conversion catalyst using a low silica to alumina
10 ratio zeolite Y bound into an extrudate and steamed to modify the catalyst.

11 U.S. Pat. No. 4,764,295 discloses a process for making non-foaming
12 detergent-dispersant lubricating oil additives. The process further involves
13 carbonation for making the products more basic.

14 U.S. Pat. No. 4,876,408 discloses an alkylation process using an ammonium-
15 exchanged and steam stabilized zeolite Y catalyst having an increased
16 selectivity for mono-alkylation the process involves the presence of at least
17 one organic compound under conditions such that sufficient amount of
18 carbonaceous material evenly deposits on the alkylation catalyst to
19 substantially suppress its alkylation activity.

20 U.S. Pat. No. 4,916,096 discloses use of a zeolite Y catalyst for
21 hydroprocessing. The zeolite Y catalyst comprises a modified crystalline
22 aluminosilicate zeolite Y, a binder and at least one hydrogenation component
23 of a Group VI or a Group VIII metal.

24 U.S. Pat. No. 5,026,941 discloses the use of a zeolite Y catalyst having a
25 silica to alumina molar ratio of 15 to 110 for the alkylation of naphthalene or
26 mono-isopropylnaphthalene.

1 U.S. Pat. No. 5,118,896 discloses an aromatic alkylation process comprising
2 the steps of contacting an aromatic hydrocarbon feed with an alkylating agent
3 under liquid phase alkylation conditions in the presence of a silica-containing
4 large macropore, small particle size zeolite catalyst, the catalyst having a pore
5 volume of about 0.25 to 0.50 cc/g in pores having a radius of 450 angstroms
6 and a catalyst particle diameter of not more than 1/32 of an inch.

7 U.S. Pat. No. 5,191,135 discloses the process for making long-chain
8 alkyl-substituted aromatic compounds from naphthalenes, the process
9 comprising a zeolite alkylation catalyst in the presence of 0.5 to 3.0 weight
10 percent water. The presence of water increases the selectivity for making
11 mono-alkylated products.

12 U.S. Pat. Nos. 5,240,889 and 5,324,877 disclose processes for the
13 preparation of a catalyst composition having alkylation and/or transalkylation
14 activity and wherein the catalyst composition contains greater than 3.5 weight
15 percent water based on the total weight of the catalyst composition and the
16 aromatic alkylation process using said catalyst composition and olefins
17 containing 2 carbon atoms to 25 carbon atoms.

18 U.S. Pat. No. 5,506,182 discloses the preparation of a catalyst composition
19 comprising 10 to 90 percent of a modified zeolite Y catalyst formed from a
20 modified zeolite Y and 10 to 90 percent binder using slurries of the modified
21 zeolite Y and the binder to form the catalyst composition having a clear
22 absorption peak in an IR spectrum of a wavelength of 3602 per centimeter.
23 The patent also discloses the substitution of iron for the alumina in the zeolite
24 Y structure.

25 U.S. Pat. No. 5,922,922 discloses a process for isomerizing a normal alpha
26 olefin in the presence of an acidic catalyst having a one-dimensional pore
27 system, and then using of the isomerized olefin to alkylate aromatic

1 hydrocarbons in the presence of a second acidic catalyst, which can be
2 zeolite Y having a silica to alumina ratio of at least 40 to 1.

3 U.S. Pat. No. 5,939,594 discloses the preparation of a superalkalinized
4 alkylaryl sulfonate of alkaline earth metal. The alkyl group of the alkylaryl
5 sulfonate contains between 14 to 40 carbon atoms and the aryl sulfonate
6 radical of alkaline earth metal is fixed in a molar proportion comprised
7 between 0 and 13% in positions 1 or 2 of the linear alkyl chain.

8 U.S. Pat. No. 6,031,144 discloses a process for reducing the residual olefin
9 content of an alkylation reaction product by removing at least a portion of the
10 non-alkylated single-ring aromatic hydrocarbon and then reacting the
11 remaining alkylation reaction product in the presence of an acidic catalyst
12 such as a molecular sieve or clay.

13 U.S. Pat. No. 6,337,310 discloses the preparation of alkylbenzene from
14 preisomerized normal alpha olefins for making low overbased and high
15 overbased sulfonates having a TBN in the range of 3 to 500. The process
16 uses HF as catalyst or a solid acidic alkylation catalyst, such as a zeolite
17 having an average pore size of at least 6 angstroms.

18 It is known that most solid acid catalysts produce high 2-aryl attachment when
19 alkylating with alpha-olefins. See S. Sivasanker, A. Thangaraj, "Distribution of
20 Isomers in the Alkylation of Benzene with Long-Chain Olefins over Solid Acid
21 Catalysts," *Journal of Catalysis*, 138, 386-390 (1992).

22 Two general treatises on zeolite are; Handbook of Molecular Sieves by
23 Rosemarie Szostak (Van Nostrand Reinhold, New York 1992) and Molecular
24 Sieves: Principles of Synthesis and Identification, 2nd Edition, by Rosemarie
25 Szostak (Chapman and Hall, London, UK 1999).

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SUMMARY OF THE INVENTION

2 The present invention is directed to zeolite Y catalysts having a controlled
3 macropore structure. The present invention is also directed to catalyst
4 composites comprising zeolite Y catalyst and a process for preparing the
5 catalyst composites. The catalysts and catalyst composites exhibit reduced
6 deactivation rates during the alkylation process, thereby increasing the life of
7 the catalysts and catalyst composites. The present invention is also directed
8 to processes for preparation of carbonated, overbased alkylated aromatic
9 sulfonates, which processes comprise the alkylation in the presence of the
10 catalysts and catalyst composites of this invention, and further sulfonation and
11 carbonation, overbasing of alkylated aromatic hydrocarbons.

12 In particular, the present invention is directed to a catalyst having a
13 macropore structure comprising zeolite Y wherein the peak macropore
14 diameter of the catalyst, measured by ASTM Test No. D 4284-03, is less than
15 or equal to about 2000 angstroms, and the cumulative pore volume at pore
16 diameters less than or equal to about 500 angstroms, measured by ASTM
17 Test No. D 4284-03, is less than or equal to about 0.30 milliliters per gram,
18 preferably less than about 0.30 milliliters per gram at pore diameters less than
19 or equal to about 400 angstroms, and more preferably in the range of about
20 0.05 milliliters per gram to about 0.18 milliliters per gram at pore diameters
21 less than or equal to about 400 angstroms.

22 The cumulative pore volume of the zeolite Y catalyst at pore diameters less
23 than or equal to about 300 angstroms is preferably less than about
24 0.25 milliliters per gram, more preferably at pore diameters less than or equal
25 to about 300 angstroms is less than about 0.20 milliliters per gram, and most
26 preferably at pore diameters less than or equal to about 300 angstroms is in
27 the range of about 0.08 milliliters per gram to about 0.16 milliliters per gram.

1 Preferably the peak macropore diameter of the zeolite Y catalyst is in the
2 range of about 700 angstroms to about 1800 angstroms, and more preferably
3 the peak macropore diameter is in the range of about 750 angstroms to about
4 1600 angstroms, and most preferably the peak macropore diameter is in the
5 range of about 800 angstroms to about 1400 angstroms.

6 The zeolite Y catalyst of the present invention may have silica to alumina ratio
7 of about 5:1 to about 100:1, preferably the silica to alumina ratio is from about
8 30:1 to about 80:1, and most preferably the silica to alumina ratio is from
9 about 50:1 to about 70:1.

10 In an embodiment of the zeolite Y catalyst of the present invention, the
11 catalyst is in the form of a tablet. The tablet may or may not include a binder.
12 Preferably the peak macropore diameter of the zeolite Y catalyst tablet is in
13 the range of about 500 angstroms to about 1500 angstroms, and the
14 cumulative pore volume at pore diameters less than or equal to about
15 500 angstroms is in the range of about 0.05 milliliters per gram to about
16 0.15 milliliters per gram.

17 An embodiment of the present invention is directed to a catalyst composite
18 comprising:

19 (a) the zeolite Y catalyst of the above invention; and

20 (b) a binder.

21 The binder in (b) above is a suitable inorganic material, preferably the binder
22 is alumina.

23 The zeolite Y in the catalyst composite of the above embodiment is in the
24 range of about 40 weight percent to about 99 weight percent based on the
25 total dry weight of the catalyst composite. Preferably, zeolite Y in the catalyst

1 composite is in the range of about 50 weight percent to about 85 weight
2 percent based on the total dry weight of the catalyst composite.

3 A further embodiment of the present invention is directed to the process for
4 preparing a catalyst composite comprising the steps of:

5 (a) contacting a zeolite Y powder with a binder in the presence of
6 volatiles to form a mixture wherein the weight ratio of the zeolite Y
7 is in the range of about 40 to about 99 based on the total dry
8 weight of the resulting catalyst composite, and wherein the volatiles
9 in the mixture are in the range of about 30 weight percent to about
10 70 weight percent;

11 (b) shaping the mixture to form a composite;

12 (c) drying the composite; and

13 (d) calcining the composite in a substantially dry environment.

14 The shaping in step (b) in the above process preferably comprises extruding.

15 The above process further comprises addition of a shaping aid in step (a).

16 Preferably, the shaping aid is a polysaccharide.

17 The binder in step (a) above is a suitable inorganic material, preferably the
18 binder is alumina.

19 The volatiles in step (a) in the process for making the zeolite Y composite
20 comprise water and an acid, and preferably the acid is nitric acid.

21 The volatiles in step (a) in the above process for making the zeolite Y
22 composite further comprise a polysaccharide.

1 The volatiles in the mixture in step (a) in the process for making the zeolite Y
2 composite are in the range of about 40 weight percent to about 60 weight
3 percent of the mixture.

4 In step (a) of the above process, the weight percent of the zeolite Y is in the
5 range of about 50 to about 85.

6 A further embodiment of the present invention is directed to a catalyst
7 composite made by the above process.

8 Another embodiment of the present invention is directed to a process for
9 making an alkylated aromatic composition comprising contacting at least one
10 aromatic hydrocarbon with at least one olefin under alkylation conditions in
11 the presence of a catalyst having a macropore structure comprising zeolite Y
12 wherein the peak macropore diameter of the catalyst, measured by ASTM
13 Test No. D 4284-03, is less than or equal to about 2000 angstroms and
14 cumulative pore volume of the catalyst at pore diameters less than or equal to
15 about 500 angstroms, measured by ASTM Test No. D 4284-03, is equal to or
16 less than about 0.30 milliliters per gram.

17 The above alkylation process is conducted without the addition of water and
18 using dried aromatic hydrocarbon and olefin feed. It is believed that the
19 presence of water during the alkylation increases the deactivation rate of the
20 catalysts of this invention.

21 The above alkylation process further comprises sulfonating the alkylated
22 aromatic composition to form an alkylated aromatic sulfonic acid.

23 The above process further comprises reacting the alkylated aromatic sulfonic
24 acid an alkaline earth metal and carbon dioxide to produce a carbonated,
25 overbased alkylated aromatic sulfonate.

1 Yet a further embodiment of the present invention is directed to a process for
2 making an alkylated aromatic composition comprising contacting at least one
3 aromatic hydrocarbon with at least one olefin under alkylation conditions in
4 the presence of a catalyst composite comprising zeolite Y, and wherein the
5 catalyst composite is prepared by the above process.

6 The aromatic hydrocarbon of the above process is benzene, toluene, xylene,
7 cumene, or mixtures thereof. Preferably, the aromatic is benzene or toluene.

8 The olefin in the above process may be an alpha olefin, an isomerized olefin,
9 a branched-chain olefin, or mixtures thereof. The olefin may have from about
10 4 carbon atoms to about 80 carbon atoms. The alpha olefin or the isomerized
11 olefin may have from about 6 carbon atoms to about 40 carbon atoms,
12 preferably from about 20 carbon atoms to about 40 carbon atoms. The
13 branched-chain olefin may have from about 6 carbon atoms to about
14 70 carbon atoms, preferably from about 8 carbon atoms to about 50 carbon
15 atoms, and more preferably from about 12 carbon atoms to about 18 carbon
16 atoms.

17 The olefin in the above process may be a partially-branched-chain olefin
18 containing from about 6 carbon atoms to about 40 carbon atoms, preferably
19 from about 20 carbon atoms to about 40 carbon atoms.

20 The above alkylation process further comprises sulfonating the alkylated
21 aromatic composition to form an alkylated aromatic sulfonic acid.

22 The above process further comprises reacting the alkylated aromatic sulfonic
23 acid an alkaline earth metal and carbon dioxide to produce a carbonated,
24 overbased alkylated aromatic sulfonate.

25 Yet a further embodiment of the present invention is directed to a process for
26 making an alkylated aromatic composition comprising contacting at least one

1 aromatic hydrocarbon with at least one olefin under alkylation conditions in
2 the presence of a catalyst composite comprising zeolite Y, and wherein the
3 catalyst composite is prepared by the above process.

4 The aromatic hydrocarbon of the above process is benzene, toluene, xylene,
5 cumene, or mixtures thereof. Preferably, the aromatic is benzene or toluene.

6 The olefin in the above process may be an alpha olefin, an isomerized olefin,
7 a branched-chain olefin, or mixtures thereof. The olefin may have from about
8 4 carbon atoms to about 80 carbon atoms. The alpha olefin or the isomerized
9 olefin may have from about 6 carbon atoms to about 40 carbon atoms,
10 preferably from about 20 carbon atoms to about 40 carbon atoms. The
11 branched-chain olefin may have from about 6 carbon atoms to about
12 70 carbon atoms, preferably from about 8 carbon atoms to about 50 carbon
13 atoms, and more preferably from about 12 carbon atoms to about 18 carbon
14 atoms.

15 The olefin in the above process may be a partially-branched-chain olefin
16 containing from about 6 carbon atoms to about 40 carbon atoms, preferably
17 from about 20 carbon atoms to about 40 carbon atoms.

18 The above alkylation process is conducted without the addition of water and
19 preferably using dried aromatic hydrocarbon and olefin feed. It is believed
20 that the presence of water during the alkylation increases the deactivation rate
21 of the catalysts of this invention.

22 The above alkylation process further comprises sulfonating the alkylated
23 aromatic composition to form an alkylated aromatic sulfonic acid.

24 The above process further comprises reacting the alkylated aromatic sulfonic
25 acid an alkaline earth metal and carbon dioxide to produce a carbonated,
26 overbased alkylated aromatic sulfonate.

1 The process of the above embodiment of the present invention for making an
2 alkylated aromatic composition further comprises the step of isomerizing
3 normal alpha olefin with an isomerizing acidic catalyst before contacting the
4 aromatic with the olefin to prepare an alkyl aromatic product where less than
5 40 weight percent of the alkylated aromatic hydrocarbon is 2-aryl, and at least
6 20 weight percent, preferably at least 75 weight percent of the alkylated
7 aromatic hydrocarbon is a mono-alkylate.

8 Preferably, the acidic catalyst in the isomerization step is a solid catalyst
9 having at least one metal oxide, which has an average pore size of less than
10 5.5 angstroms. More preferably, that acidic catalyst is a molecular sieve with
11 a one-dimensional pore system.

12 DETAILED DESCRIPTION OF THE INVENTION

13 DEFINITIONS

14 The term "alkylate" means an alkylated aromatic hydrocarbon.

15 The term "2-aryl content" is defined as the percentage of total alkylate (the
16 alkylate species in which the alkyl chain attached to the aromatic ring is
17 derived from the olefin employed in the present alkylation process) that is
18 comprised of those chemical species in which the attachment of the alkyl
19 chain to the aromatic ring is at the 2-position along the alkyl chain.

20 The term "binder" means any suitable inorganic material which can serve as
21 matrix or porous matrix to bind the zeolite particles into a more useful shape.

22 The term "branched-chain olefins" means olefins derived from the
23 polymerization of olefin monomers higher than ethylene and containing a
24 substantial number of branches wherein the branches are alkyl groups having
25 from about one carbon atom to about 30 carbon atoms. Mixtures of ethylene
26 and higher olefins are also contemplated.

1 The term "calcining" as used herein means heating the catalyst to about
2 400°C to about 1,000°C in a substantially dry environment.

3 The term "carbonated, overbased" is used to describe those alkaline earth
4 metal alkyl aromatic sulfonates in which the ratio of the number of equivalents
5 of the alkaline earth metal moiety to the number of equivalents of the aromatic
6 sulfonic acid moiety is greater than one, and is usually greater than 10 and
7 may be as high as 20 or greater.

8 The term "centrate" refers to a mixture of sludge fractions that were collected
9 from prior carbonation, overbasing of alkylbenzene sulfonic acids similar to
10 the sulfonic acids of the present invention. Centrate was produced during the
11 purification of high TBN carbonated, overbased synthetic sulfonates by
12 centrifugation and decantation at the end of the carbonation, overbasing
13 reaction. Centrate was added to the carbonation, overbasing of alkylbenzene
14 sulfonic acid reaction mixture in Example 11 in this patent application for
15 recycling the contents of the centrate. Prior to its addition to the reaction
16 mixture in Example 11, the centrate was characterized by determination of its
17 TBN, the amount of xylene solvent, active calcium sulfonate, calcium
18 hydroxide, calcium carbonate, carbon dioxide and 100 Neutral diluent oil.

19
20 The term "cumulative pore volume" obtained by Mercury Intrusion Porosimetry
21 as used herein refers to that part of the total volume in milliliters per gram
22 derived from the graphical, cumulative pore volume distribution, measured by
23 Section 14.1.6 of ASTM D 4284-03, or the corresponding tabular presentation
24 of the same data between defined upper and lower pore diameters. When no
25 lower diameter limit is defined, the lower limit is the lowest detection limit or
26 lowest radius measured by Section 14.1.6 of ASTM D 4284-03.

27 The terms "dry basis", "anhydrous basis", and "volatiles-free basis" shall refer
28 to the dry weight of catalyst composite or raw materials expressed on a metal
29 oxides basis such as $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x \text{SiO}_2$.

1 The term "loss-on-ignition (LOI)" as used herein means the percent weight
2 loss of the zeolite composite or raw material samples when they are heated to
3 538°C for 1 hour. When the temperature is greater than or equal to about
4 538°C, the "loss-on-ignition" approximates the percent volatiles.

5 The terms "macropore", "mesopore", and "micropore" as used herein follow
6 the definitions set forth by the International Union of Pure and Applied
7 Chemistry (IUPAC), Division of Physical Chemistry, in Manual of Symbols and
8 Terminology for Physicochemical Quantities and Units, Appendix II
9 Definitions, Terminology and Symbols in Colloid and Surface Chemistry Part I,
10 Adopted by the IUPAC Council at Washington, D.C., U.S.A., on 23 July, 1971.
11 Pores with widths or diameters exceeding ~50 nanometers (500 angstroms)
12 are called "macropores". Pores with widths or diameters not exceeding
13 ~2.0 nanometers (20 angstroms) are called "micropores". Pores of
14 intermediate size (2.0 nanometers < width or diameter ≤ 50 nanometers) are
15 called "mesopores".

16 The term "Mercury Intrusion Porosimetry" refers to the ASTM Test
17 No. D 4284-03 used to determine pore volume distribution of catalysts by
18 Mercury Intrusion Porosimetry. Mercury pore distribution was measured
19 using a Quantachrome Scanning Mercury Porosimeter Model SP-100. The
20 software version used by the instrument is V2.11 (dated 10/27/93). Surface
21 tension used in the calculation is 473 dynes per centimeter and the contact
22 angle is 140 degrees.

23 The terms "normal alpha olefin" and "linear alpha olefin" mean those
24 straight-chain olefins without a significant degree of alkyl branching in which
25 the carbon to carbon double bond resides primarily at the end or "alpha"
26 position of the carbon chain, i.e., between C₁ and C₂. Normal alpha olefins
27 are derived from polymerization of ethylene.

1 The term "normal alpha olefin isomerization" means the conversion of normal
2 alpha olefins into isomerized olefins having a lower alpha olefin content (the
3 double bond is between C₁ and C₂), higher internal olefin content (the double
4 bond is in positions other than between C₁ and C₂), and optionally a higher
5 degree of branching.

6 The term "partially-branched chain olefin" is defined as the olefin product of
7 isomerization of normal alpha olefins wherein the degree of branching is
8 higher than in the starting normal alpha olefins.

9 The term "peak macropore diameter" as used herein means the peak
10 diameter (i.e., the diameter within the macropore region at which the
11 differential plot of pore size distribution, as defined by Section 14.2, reaches a
12 maximum) in the macropore range determined by ASTM Test No. D 4284-03
13 for the macropore peak in the catalysts of the present invention.

14 The term "peptizing" means the dispersion of large aggregates of binder
15 particles, including hydrated aluminas, into much smaller primary particles by
16 the addition of acid.

17 The term "percent volatiles" as used herein means the difference between the
18 actual weight of the catalyst composite or the raw materials and the weight of
19 the material on a dry, anhydrous, or volatiles-free basis, expressed as a
20 percentage of the actual sample weight.

21 The terms "SAR" or "silica to alumina ratio" refer to the molar ratio of silicon
22 oxide to aluminum oxide; mol SiO₂:mol AlO₃.

23 The term "sufficient water to shape the catalyst material" means quantity of
24 water required to make an acid peptized mixture of zeolite and alumina
25 powders into an extrudable mass.

1 The term "tableting" as used herein refers to the process of forming a catalyst
2 aggregate from zeolite powder or a mixture of zeolite and binder powders by
3 compressing the powder in a die.

4 The term "total base number or TBN" refers to the amount of base equivalent
5 to milligrams of KOH in one gram of sample. Thus, higher TBN numbers
6 reflect more alkaline products, and therefore a greater alkalinity reserve. The
7 TBN of a sample can be determined by ASTM Test No. D 2896 or any other
8 similar procedure.

9
10 The term "total pore volume" obtained by Mercury Intrusion Porosimetry as
11 used herein refers to the total pore volume in milliliters per gram derived from
12 the graphical, cumulative pore volume distribution (Section 14.1.6 of ASTM
13 D 4284-03) or the corresponding tabular presentation of the same data.

14 As used herein, all percentages are weight percent, unless otherwise
15 specified.

16 As noted above, the present invention is directed to catalyst having a
17 controlled macropore structure comprising zeolite Y. The catalysts of the
18 present invention were characterized by pore volume distribution obtained by
19 Mercury Intrusion Porosimetry, ASTM Test No. D 4284-03. Mercury Intrusion
20 Porosimetry provides a graph of cumulative pore volume (pv) versus pore
21 diameter (pd). Mercury Intrusion Porosimetry also is used to determine the
22 macropore peak diameter from the derivative, delta pv (Δpv) divided by delta
23 pd (Δpd). The graphs are used to characterize the catalysts of the present
24 invention.

25 Zeolite Y catalysts and catalyst composites of the present invention when
26 used in alkylation of aromatic hydrocarbons with olefins exhibited a
27 substantial reduction in deactivation rates compared to zeolitic catalysts
28 known in the prior art. This result was unexpected, since it had previously

1 been believed that increasing the surface area of the catalyst would increase
2 its activity, but was likely to also increase deactivation rates. Relative
3 deactivation rates were determined for the catalysts of the present invention
4 under standard alkylation reactions conditions. Results of the deactivation
5 experiments are given in Table II. Reduction in deactivation rates of up to
6 75 percent and above were observed during alkylation reactions using these
7 zeolitic Y catalysts and zeolite Y catalyst composites.

8 The zeolite Y catalysts and catalyst composites can be prepared using zeolite
9 Y CBV 760® or CBV 600® available from Zeolyst International. Samples of
10 these zeolite Y materials from which catalysts and catalyst composites of the
11 present invention were prepared had a nominal silica to alumina ratio of ~60:1
12 and ~6.7:1, respectively. However, zeolite Y having a silica to alumina ratio
13 between 5:1 and 120:1 may be used for the preparation of the zeolite Y
14 catalysts and catalyst composites of the present invention.

15 The zeolite Y catalysts of the present invention may be shaped or formed into
16 tablets, extrudates or any other shape using procedures well known in the
17 prior art. The preparation of extrudates requires the presence of a binder,
18 such as alumina. The tabletted catalysts do not require the presence of a
19 binder, but a binder may be present in a tabletted zeolite catalyst. The
20 crystalline zeolite powder may be compressed to form a tablet. The tabletted
21 catalysts of the present invention provide exceptionally low deactivation rates
22 in alkylation reactions.

23 The alkylation reaction may be carried out by any conventionally known
24 process without the addition of water and using a dried aromatic hydrocarbon
25 and olefin feed. It is believed that the presence of water during the alkylation
26 increases the deactivation rate of the catalysts of this invention. The aromatic
27 hydrocarbon is reacted with one or more olefins in the presence of a catalyst
28 of the present invention under alkylation reaction conditions. The aromatic
29 hydrocarbon may be single-ring or double-ring, preferably the aromatic

1 hydrocarbon is a single-ring aromatic hydrocarbon. The aromatic
2 hydrocarbon may be an alkylated aromatic hydrocarbon, such as a
3 mono-alkylated aromatic hydrocarbon, wherein the alkyl group has from about
4 4 carbon atoms to about 80 carbon atoms. When the aromatic hydrocarbon
5 used is a mono-alkylated aromatic, the product of the alkylation reaction is a
6 di-alkylated aromatic.

7 The olefins useful for alkylation of the aromatic hydrocarbons may be
8 linear-chain olefins or branched-chain olefins having from about 4 carbon
9 atoms to about 80 carbon atoms. In addition, normal alpha olefins may be
10 isomerized to obtain partially-branched-chain olefins for use in alkylation
11 reaction of the present invention. These resulting partially-branched-chain
12 olefins may be alpha-olefins, beta-olefins, internal-olefins, tri-substituted
13 olefins, and vinylidene olefins.

14 Alkylated aromatic hydrocarbon sulfonic acids of the alkylated aromatic
15 hydrocarbons of the present invention may be prepared by any known
16 sulfonation reaction. The alkylated aromatic sulfonic acids may be further
17 reacted with an alkaline earth metal and carbon dioxide to obtain carbonated,
18 overbased alkylated aromatic sulfonates useful as detergents in lubricating
19 oils. Carbonation may be carried out by any conventionally known process.
20 The degree of overbasing may be controlled by changing the reaction
21 conditions and the amount of the alkaline earth metal and carbon dioxide
22 used in the carbonation process.

23 Procedure for Isomerization of Normal Alpha Olefins

24 The isomerization process may be carried out in batch or continuous mode.
25 The process temperatures can range from 50°C to 250°C. In the batch mode,
26 a typical method is to use a stirred autoclave or glass flask, which may be
27 heated to the desired reaction temperature. A continuous process is most

1 efficiently carried out in a fixed bed process. Space rates in a fixed bed
2 process can range from 0.1 to 10 or more weight hourly space velocity.

3 In a fixed bed process, the isomerization catalyst is charged to the reactor and
4 activated or dried at a temperature of at least 150°C under vacuum or flowing
5 inert, dry gas. After activation, the temperature of the isomerization catalyst is
6 adjusted to the desired reaction temperature and a flow of the olefin is
7 introduced into the reactor. The reactor effluent containing the partially-
8 branched, isomerized olefins is collected. The resulting partially-branched,
9 isomerized olefins contain a different olefin distribution (alpha olefin, beta
10 olefin; internal olefin, tri-substituted olefin, and vinylidene olefin) and
11 branching content than the unisomerized olefin.

12 Procedure for Alkylation of Aromatic Hydrocarbons

13 Alkylation of aromatic hydrocarbons with normal alpha olefins, partially-
14 branched-chain isomerized olefins, and branched-chain olefins may be
15 carried out by any method known by a person skilled in the art.

16 The alkylation reaction is typically carried out with an aromatic hydrocarbon
17 and an olefin in molar ratios from 1:15 to 25:1. Process temperatures can
18 range from about 100°C to about 250°C. The process is carried out without
19 the addition of water. As the olefins have a high boiling point, the process is
20 preferably carried out in the liquid phase. The alkylation process may be
21 carried out in batch or continuous mode. In the batch mode, a typical method
22 is to use a stirred autoclave or glass flask, which may be heated to the
23 desired reaction temperature. A continuous process is most efficiently carried
24 out in a fixed bed process. Space rates in a fixed bed process can range from
25 0.01 to 10 or more weight hourly space velocity.

26 In a fixed bed process, the alkylation catalyst is charged to the reactor and
27 activated or dried at a temperature of at least 150°C under vacuum or flowing

1 inert, dry gas. After activation, the alkylation catalyst is cooled to ambient
2 temperature and a flow of the aromatic hydrocarbon compound is introduced,
3 optionally toluene. Pressure is increased by means of a back pressure valve
4 so that the pressure is above the bubble point pressure of the aromatic
5 hydrocarbon feed composition at the desired reaction temperature. After
6 pressurizing the system to the desired pressure, the temperature is increased
7 to the desired reaction temperature. A flow of the olefin is then mixed with the
8 aromatic hydrocarbon and allowed to flow over the catalyst. The reactor
9 effluent comprising alkylated aromatic hydrocarbon, unreacted olefin and
10 excess aromatic hydrocarbon compound are collected. The excess aromatic
11 hydrocarbon compound is then removed by distillation, stripping, evaporation
12 under vacuum, or any other means known to those skilled in the art.

13 Procedure for Sulfonation of Alkylated Aromatic Hydrocarbons

14 Sulfonation of alkylated hydrocarbons may be carried out by any method
15 known by a person skilled in the art.

16 The sulfonation reaction is typically carried out in a falling film tubular reactor
17 maintained at about 65°C. The alkylated aromatic hydrocarbon is placed in
18 the tube and sulfur trioxide diluted with nitrogen is added to the alkylated
19 aromatic hydrocarbon. The molar ratio of alkylated aromatic hydrocarbon to
20 sulfur trioxide is maintained at about 1.05:1. The resulting alkylated aromatic
21 sulfonic acid may be diluted with about 10% 100 Neutral oil followed by
22 thermal treatment with nitrogen bubbling at a rate of about 10 liters per
23 kilogram of product and stirring while maintaining the temperature at about
24 85°C until the desired residual sulfuric acid content is obtained (maximum of
25 about 0.5%).

1 Procedure for Carbonation, Overbasing of Alkylated Aromatic Sulfonic acids

2 Carbonation, overbasing of alkylaromatic sulfonic acids may be carried out by
3 any method known by a person skilled in the art to produce alkylaromatic
4 sulfonates.

5

6 Generally, the carbonation, overbasing reaction is carried out in a reactor in
7 the presence of the alkylated aromatic sulfonic acid, diluent oil, an aromatic
8 solvent, and an alcohol. The reaction mixture is agitated and alkaline earth
9 metal and carbon dioxide are added to the reaction while maintaining the
10 temperature between about 20°C and 80°C.

11

12 The degree of carbonation, overbasing may be controlled by the quantity of
13 the alkaline earth metal and carbon dioxide added to the reaction mixture, the
14 reactants and the reaction conditions used during the carbonation process.

15 EXAMPLES

16 Preparation of Zeolite Y Alkylation Catalyst Composite

17 Example 1

18 Preparation of Catalyst Composite 1

19 Zeolite Y alkylation catalyst composites were prepared by the following
20 method:

21 Loss-on-ignition (LOI) was determined for a sample of a commercially
22 available zeolite Y CBV 760® available from Zeolyst International by heating
23 the sample to 538°C for 1 hour. The LOI obtained was 14.65 weight % and
24 provided the percent volatiles in the zeolite Y batch being used. The LOI of a
25 commercial sample of Versal® hydrated aluminum oxide available from
26 Kaiser LaRoche Hydrate Partners was determined by heating the sample to

1 538°C for 1 hour and was 24.87 weight %. Next, based on the results
2 obtained from the LOI, 1875 grams of zeolite Y powder and 532 grams of
3 alumina powder were weighed out to give a total of 1600 grams of zeolite
4 powder and 400 grams of alumina powder on a volatile-free basis. Extrusion
5 aid, Methocell®, 60 grams, available from Dow Corning, was added to the
6 mixture of the two powders.

7 The two dry powders were added to a Baker Perkins mixer and dry mixed for
8 4 minutes. The amount of concentrated (70.7%) nitric acid to give
9 0.7 weight % (based on 100% nitric acid) of the dry weight of the zeolite and
10 the alumina powders was calculated to be 19.8 grams. This amount of 70.7%
11 nitric acid was weighed out and dissolved in 200 grams of deionized water.

12 The total amount of water and 70.7% nitric acid needed to obtain a final
13 concentration of approximately 50% total volatiles was calculated as follows.
14 Volatiles in the Y zeolite powder are 274.67 grams (1874.67 gram total
15 weight – 1600 grams dry weight). Volatiles in the alumina powder are
16 232.40 grams (532.4 grams total weight – 400 grams dry weight). Nitric acid
17 solution and Methocell® extrusion aid are considered to be 100% volatiles.
18 Thus, if all the above raw materials were combined, the volatiles would be
19 786.87 grams. To give a mixture of 2000 grams (1600 grams zeolite and
20 400 grams alumina) dry powder with 50% volatiles, the total weight of the
21 mixture must be 4000 grams. Thus, an additional 1213.13 grams of deionized
22 water must be added.

23 To the powders in the mixer, 1250 grams of deionized water were added over
24 a period of 5 minutes using a peristaltic pump. The mixer was then stopped
25 so that the walls of the mixer could be scraped down. Mixing was then
26 resumed and the solution of nitric acid in water was added over 5 minutes
27 using the peristaltic pump. At the end of acid addition, mixing was continued
28 for a total time of 40 minutes, with occasional holds to allow for scraping the
29 sides of the mixer. At the end of the mixing period, the mixture was still

1 powdery and the volatiles were measured as 48.83 weight %. Additional
2 amounts of deionized water 10 grams at a time were added with 5 minutes
3 mixing for each addition until the mixture appeared extrudable. A total of
4 85 grams of additional water was added over 1 hour and 45 minutes. At this
5 point, the volatiles were 48.36 weight %.

6 The wet mixture was extruded through 1.27 millimeters, asymmetric
7 quadrilobe die inserts, in a Bonnot extruder. The wet long cylindrical strands
8 were dried at 121°C for 8 hours. The long cylindrical strands were then
9 broken to give extrudates with length to diameter ratio of 2:6. The extrudates
10 were sieved and the portion larger than 1 millimeter was retained.

11 The extrudates were then calcined in a substantially dry environment in a
12 muffle furnace using the following temperature program:

13 The extrudates were heated to 593°C over two hours, then held at 593°C for
14 1/2 hour and next cooled to 204°C. A total of 1681 grams of extrudates were
15 obtained.

16 Mercury Intrusion Porosimetry showed the extrudates to have a peak
17 macropore diameter of 1167 angstroms and a cumulative pore volume at
18 diameters less than 300 angstroms of 0.1400 ml/gram.

19 Example 2

20 Preparation of Catalyst Composite 2

21 Zeolite Y catalyst was prepared following the procedure used in Example 1
22 above, with the following exceptions:

23 Catapal B® alumina available from Vista Chemical Company was used
24 instead of Versal® alumina. The total amount zeolite Y and alumina powders
25 were scaled to 1300 grams dry weight. Methocell® extrusion aid was not
26 added. Volatiles of the zeolite powder and alumina powder were

1 9.72 weight % and 24.82 weight %, respectively. Concentrated nitric acid,
2 12.9 grams, was dissolved in 300 grams deionized water. In the Baker
3 Perkins mixer, 671.7 grams of deionized water were added in 10 minutes,
4 followed by the acid solution in 10 minutes. After mixing for 40 minutes,
5 volatiles were 47.18 weight %, but the mixture was too thick to extrude. With
6 an additional 3 hours of mixing, the mixture was still not extrudable. Over the
7 next 30 minutes, an additional 10 grams of deionized water was added. The
8 mixture was then extruded, dried, and calcined in a substantially dry
9 environment.

10 Mercury Intrusion Porosimetry showed the peak macropore diameter to be
11 878 angstroms and the cumulative pore volume at diameters less than
12 300 angstroms to be 0.1424 ml/gram.

13 Example 3

14 Preparation of Catalyst Composite 3

15 This catalyst was made by the procedure described in Example 2 above with
16 the following exceptions:

17 Volatiles of the zeolite Y powder and alumina powder were 12.24 weight %
18 and 23.89 weight %, respectively. Corresponding amounts of zeolite and
19 alumina powders were 1185 grams and 342 grams, respectively. Added
20 deionized water was 580 grams. After 50 minutes of mixing, the mixture was
21 still granular. A good paste was obtained after mixing for 1 hour 30 minutes.
22 Volatiles were 46.8 weight % at extrusion time. After extruding, drying, sizing,
23 and calcining in a substantially dry environment, Mercury Intrusion
24 Porosimetry showed the peak macropore diameter to be 1006 angstroms and
25 the cumulative pore volume at diameters less than 300 angstroms to be
26 0.1400 ml/gram.

1
2

Example 4
Preparation of Catalyst Composite 4

3 This catalyst was made by the procedure described in Example 2 with the
4 following exceptions:

5 Volatiles of the zeolite Y powder and alumina powder were 14.36 weight %
6 and 27.54 weight %, respectively. Corresponding amounts of zeolite and
7 alumina powders were 747.4 grams and 220.8 grams, respectively. The final
8 weight % of the nitric acid of the dry weight of the zeolite and the alumina in
9 this preparation was 0.75%. The acid was dissolved in 655.8 grams of
10 deionized water. The powders were mixed in a plastic bag for 3 minutes and
11 then mixed in the Baker Perkins mixer for 3 minutes. The acid solution was
12 pumped in over 8 minutes while continued mixing. At 10 minutes after
13 completion of acid addition, the mixture became pasty. Mixing was continued
14 for an additional 30 minutes. Volatiles were 49.0 weight %. The wet mix was
15 extruded, dried, and sized.

16 The extrudates were calcined in a substantially dry environment in a muffle
17 furnace according to the following temperature program:

18 The extrudates were heated at full power to 593°C. Temperature overshoot
19 was avoided. Next, the extrudates were held at 593°C for one hour and
20 cooled to 149°C. Mercury Intrusion Porosimetry showed the peak macropore
21 diameter to be 1486 angstroms and the cumulative pore volume at diameters
22 less than 300 angstroms to be 0.1494 ml/gram.

23
24

Example 5
Preparation of Catalyst 5

25 Tabletted zeolite Y catalyst was prepared by a custom catalyst manufacturer
26 using a sample of the zeolite Y CBV 760® available from Zeolyst

1 International. The tablets were cylinders, 1/8 inch in diameter and
2 approximately 1/8 inch in length. Mercury Intrusion Porosimetry showed the
3 peak macropore diameter to be 815 angstroms and the cumulative pore
4 volume at diameters less than 300 angstroms to be 0.0844 ml/gram.

5 Example 6
6 Preparation of Catalyst 10

7 This catalyst was made by the procedure described in Example 2 with the
8 following exceptions:

9 Volatiles of the zeolite Y powder and alumina powder were 18.7 weight % and
10 26.5 weight %, respectively. Corresponding amounts of zeolite and alumina
11 powders were 639.6 grams and 276.9 grams, respectively. The final
12 weight % of the nitric acid of the dry weight of the zeolite and the alumina in
13 this preparation was 0.75% and 6.44 grams of nitric acid was dissolved in
14 150 grams of deionized water. The powders were mixed in a plastic bag for
15 15 minutes and then mixed in the Baker Perkins mixer for 10 minutes. An
16 additional 276.9 grams of deionized water was pumped into the mixture over
17 20 minutes while mixing. The acid solution was pumped in over 8 minutes
18 with continued mixing. Mixing was continued for an additional 30 minutes.
19 Volatiles were 46.40 weight %. The wet mix was extruded, dried, and sized.

20 The extrudates were calcined in a substantially dry environment in a muffle
21 furnace according to the following temperature program:

22 The extrudates were heated at full power to 593°C. Temperature overshoot
23 was avoided. Next, the extrudates were held at 593°C for one hour and
24 cooled to 149°C. Mercury Intrusion Porosimetry showed the peak macropore
25 diameter to be 941 angstroms and the cumulative pore volume at diameters
26 less than 300 angstroms to be 0.155 ml/gram.

Example 7
Preparation of Catalyst 12

This catalyst was made by the procedure described in Example 2 with the following exceptions:

Volatiles of the zeolite powder and alumina powder were 12.24 weight % and 23.89 weight %, respectively. Corresponding amounts of zeolite and alumina powders were 1185.1 grams and 341.6 grams, respectively. The final weight % of the nitric acid of the dry weight of the zeolite and the alumina in this preparation was 0.75% and 12.9 grams of nitric acid was dissolved in 300 grams of deionized water. The powders were mixed in a plastic bag for 5 minutes and then mixed in the Baker Perkins mixer for 5 minutes. Additional deionized water, 619.7 grams, was added to the mixture over 20 minutes. The acid solution was pumped in over 8 minutes with continued mixing. Mixing was continued for an additional 40 minutes. At this time, the mixture was still a powder. After 3 hours of mixing, an additional 50 grams of deionized water was added to the mixture. After 3-1/2 hours of mixing, an additional 25 grams of deionized water was added to the mixture and another 15 grams of deionized water was added to the mixture after 4 hours and 4-1/4 hours of mixing. After 4 hours and 55 minutes of mixing, the volatiles were 45.2 weight %. The wet mix was extruded, dried, and sized.

The extrudates were calcined in a substantially dry environment in a muffle furnace according to the following temperature program:

The extrudates were heated at full power to 593°C. Temperature overshoot was avoided. Next, the extrudates were held at 593°C for one hour and cooled to 149°C. Mercury Intrusion Porosimetry showed the peak macropore diameter to be 900 angstroms and the cumulative pore volume at diameters less than 300 angstroms to be 0.144 ml/gram.

1 The Mercury Intrusion Porosimetry results for the zeolite Y catalysts of
2 Examples 1-7 (Catalyst Composites 1-5, 10 and 12) are given below in
3 Table I.

4 Table I

	Mercury Intrusion Porosimetry Properties		
Catalyst Composite	Total PV* (ml/gram)	PV <300 angstroms** (ml/gram)	Macropore peak diameter (angstroms)
1	0.4612	0.140	1167
2	0.4207	0.142	878
3	0.4208	0.140	1006
4	0.4492	0.149	1486
5***	0.3914	0.084	815
10	0.403	0.155	941
12	0.399	0.144	900

5
6 * Total pore volume.
7 ** Total pore volume at diameters less than or equal to 300 angstroms.
8 *** Catalyst 5 is not a composite. Catalyst 5 is a tabletted zeolite Y powder,
9 prepared as described above in Example 5.

10

11 Example 8

12 Preparation of Isomerized Normal Alpha Olefins

13 Typically, isomerization of normal alpha olefins is carried out as described
14 below:

15 C₂₀-C₂₄ normal alpha olefin with the following composition was used for this
16 Example:

17 Alpha olefin 89.1%

18 Beta olefin 0.5%

- 1 Internal olefin 1.4%
- 2 Tri-substituted olefin 0.2%
- 3 Vinylidene olefin 9.5% (determined by carbon nuclear magnetic
- 4 resonance spectroscopy)
- 5 Branched-chain olefin 11% (determined by infra red spectroscopy)
- 6

7 The normal alpha olefin was pumped up-flow through a fixed-bed reactor
8 (570 millimeters high and with an inside diameter of 22.3 millimeters)
9 containing 65 grams of solid olefin isomerization. The reactor was operated
10 isothermally at 160°C at a liquid to hourly space velocity of 0.5 per hour and at
11 atmospheric pressure.

12 The reactor effluent containing the partially branched, isomerized olefin is
13 collected. The resulting partially-branched, isomerized olefin contains a
14 different olefin distribution (alpha-olefin, beta-olefin; internal-olefin,
15 tri-substituted-olefin, and vinylidene-olefin) and branching content than the
16 un-isomerized olefin.

17 Example 9
18 Preparation of alkylbenzene compositions

19 Typically, alkylation of aromatic hydrocarbons with normal alpha olefins,
20 partially-branched-chain isomerized olefins and branched-chain olefins was
21 carried out as described below:

22 A fixed bed reactor constructed from 15.54 millimeters internal diameter
23 Schedule 160 stainless steel pipe was used for this alkylation test. Pressure
24 in the reactor was maintained by an appropriate back pressure valve. The
25 reactor and heaters were constructed so that adiabatic temperature control
26 could be maintained during the course of alkylation runs. A 192 gram bed of
27 850 micrometer to 2 millimeters Alundum particles was packed in the bottom
28 of the reactor to provide a pre-heat zone. Next, 100 grams of Catalyst

1 Composite 12 was charged to the fixed bed reactor. The reactor was gently
2 vibrated during loading to give a maximum packed bulk density of catalyst in
3 the reactor. Finally, void spaces in the catalyst bed were filled with 351 grams
4 150 micrometers Alundum particles as interstitial packing.

5

6 The reactor was then closed, sealed, and pressure tested under nitrogen.
7 Next the alkylation catalyst was dehydrated during 15 hours at 200°C under a
8 20 liters per hour flow of nitrogen measured at ambient temperature and
9 pressure and then cooled to 100°C under nitrogen. Benzene was then
10 introduced into the catalytic bed in an up-flow manner at a flow rate of
11 195 grams per hour. Temperature (under adiabatic temperature control) was
12 increased to a start-of-run temperature of 182°C (measured just before the
13 catalyst bed) and the pressure was increased to 14.6 atmospheres.

14

15 When temperature and pressure had lined out at desired start-of-run
16 conditions of 182°C and 14.6 atmospheres, a feed mixture, consisting of
17 benzene and C₂₀₋₂₄ NAO at a molar ratio of 10:1 and dried over activated
18 alumina, was introduced in an up-flow manner. As the feed reached the
19 catalyst in the reactor, reaction began to occur and internal catalyst bed
20 temperatures increased above the inlet temperature. After about 8 hours
21 on-stream, the reactor exotherm was 20°C. At 26 hours on-stream, the olefin
22 conversion in the product was 99.1%. The run was stopped after 408 hours
23 on-stream, although the run could have continued. At this time, the olefin
24 conversion was 99.45%.

25

26 Alkylated aromatic hydrocarbon products containing excess benzene were
27 collected during the course of the run. After distillation to remove excess
28 aromatic hydrocarbon, analysis showed that greater than 99% conversion of
29 olefin was achieved during the course of the run.

30

Example 10

Preparation of alkylated benzene sulfonic acids

The alkylbenzene alkylate produced as in Example 9 above was sulfonated by a concurrent stream of sulfur trioxide (SO_3) and air with in a tubular reactor (2 meters long and 1 centimeter inside diameter) in a down flow mode using the following conditions:

Reactor temperature was 60°C , SO_3 flow rate was 73 grams per hour, alkylate flow rate was 327 grams per hour at a SO_3 to alkylate molar ratio of 1.05. The SO_3 was generated by passing a mixture of oxygen and sulfur dioxide (SO_2) through a catalytic furnace containing vanadium oxide (V_2O_5).

The resulting crude alkylbenzene sulfonic acid had the following properties based on the total weight of the product: the weight % of HSO_3 was 16.1 and the weight % of H_2SO_4 was 1.35.

The crude alkylbenzene sulfonic acid was diluted with 10 weight % 100 Neutral diluent oil based on the total weight of the crude alkylbenzene sulfonic acid and placed in a four liter four-neck glass reactor fitted with a stainless steel mechanical agitator rotating at between 300 and 350 rpm, a condenser and a gas inlet tube (2 millimeters inside diameter) located just above the agitator blades for the introduction of nitrogen gas. The contents of the reactor was heated to 85°C with stirring and nitrogen gas was bubbled through the mixture between 30-40 liters per hour for between about 4 to 6 hours until the weight % of H_2SO_4 is less than about 0.3 weight % based on the total weight of the product. This material is the final alkylbenzene sulfonic acid.

The final alkylbenzene sulfonic acid had the following properties based on the total weight of the product: weight % of HSO_3 was 15.76 and weight % of H_2SO_4 was 0.15.

Example 11

Preparation of carbonated, overbased alkylated benzene sulfonates

To a 5 liter four-neck reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at between 300 and 350 rpm, a gas inlet tube (2 millimeters inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column and condenser under nitrogen gas was charged 123.7 grams of centrate.

The centrate was a mixture of the sludge fractions previously produced during the purification of high TBN carbonated, overbased synthetic sulfonates by centrifugation and decantation and was added to the reaction mixture of this example for recycling the contents of the centrate. The centrate had a TBN of 206 and contained approximately 68 grams of xylene solvent, 11 grams active calcium sulfonate, 8 grams calcium hydroxide and calcium carbonate, 8 grams of carbon dioxide, and 22 grams of 100 Neutral diluent oil isolated.

Next, 40 grams of methanol, 207 grams of xylene solvent, 281 grams (0.59 mole) of the alkylbenzene sulfonic acid (HSO₃ was 15.8 weight % based on the total weight of the reaction mixture) from Example 10 above was charged to the reactor over 15 minutes at room temperature. A slurry of 160 grams (2.16 mole) of calcium hydroxide, 365 grams of xylene solvent, and 94.2 grams of methanol was added to the reactor and the reactor was cooled to 25°C. Next, 35 grams (0.79 mole) of CO₂ was added to the reaction mixture through the gas inlet tube over 39 minutes while the temperature of the reactor increased to about 32°C. A second slurry composed of 160 grams (2.16 mole) of calcium hydroxide, 384 grams xylene solvent, and 131 grams of methanol was then added to the reactor concurrently with 0.9 grams of CO₂ over about 1 minute. Next, 92 grams of CO₂ was added to the reactor over 64 minutes while the temperature of the reactor increased from about 30°C to 41°C. A third slurry composed of 82 grams of calcium hydroxide and 298 grams of xylene solvent was then charged to the reactor concurrently with

1 1.4 grams of CO₂ over about 1 minute. Next, 55 grams (1.25 mole) of CO₂
2 was added to the reactor over approximately 60 minutes while keeping the
3 reactor temperature at approximately 38°C.

4
5 The water and methanol were then distilled from the reactor by first heating
6 the reactor to 65°C over 40 minutes at atmospheric pressure, then to 93°C
7 over 60 minutes at atmospheric pressure, and then 130°C over 30 minutes at
8 atmospheric pressure. The temperature of the reactor was then decreased to
9 110°C over 60 minutes at atmospheric pressure and next held at 110°C for
10 30 minutes at atmospheric pressure. The contents of the reactor were then
11 cooled to approximately 30°C and 510 grams of 600 Neutral diluent oil was
12 added to the reactor followed by 413 grams of xylene solvent. The sediment
13 in the product was then removed by centrifugation. The xylene solvent in the
14 product was distilled by heating the product to 204°C over approximately
15 45 minutes at 30 millimeters Hg vacuum and holding the product at 204°C
16 and 30 millimeters Hg vacuum for 10 minutes. The vacuum was replaced
17 with nitrogen gas and the contents were allowed to cool to room temperature
18 to afford the carbonated, overbased sulfonate with the following properties
19 based on the total weight of the product:

20
21 Weight % calcium was 16.1, TBN was 424, weight % of sulfur was 1.81,
22 weight % of calcium sulfonate was 0.87, and viscosity was 101 cSt at 100°C.

23
24 Example 12
25 Procedure for Measuring Deactivation Rates of the Catalysts
26 in Alkylation Reactions

27 Deactivation rates of the alkylation catalysts were measured during the
28 alkylation reaction similar to the alkylation reaction in Example 9 above.

29 The alkylation reaction was carried out as described above under adiabatic
30 temperature control. As the alkylation reaction was exothermic, a

1 temperature exotherm was measured by means of appropriately located
 2 thermocouples in the catalyst bed. Using temperature profile data from a
 3 catalyst run, the position of the temperature exotherm in the bed was plotted
 4 as a function of time, in hours. The deactivation rate of the catalyst is the
 5 slope of this line in centimeters per hour. All catalysts were evaluated at
 6 standard conditions of temperature, pressure, and space velocity and the
 7 deactivation rates were measured.

8 Catalyst Composites 1, 2, 4, 5, 10 and 12 are the Catalyst Composites
 9 prepared in Examples 1-7 and shown in Table I above with the exception that
 10 Catalyst Composite 2 in Table II is a mixture of batches of Catalyst
 11 Composite 2 in Table I.

12 Test 1 was conducted during alkylation of toluene with an isomerized C₂₀ to
 13 C₂₄, low alpha content olefin at a temperature of 170°C. The molar ratio of
 14 toluene to olefin was 6.

15 Test 2 was conducted during alkylation of benzene with a C₂₀ to C₂₄ normal
 16 alpha olefin at a temperature of 180°C. The molar ratio of toluene to olefin
 17 was 10.

18 Deactivation rates are shown relative to the deactivation rate of Catalyst
 19 Composite 8 and Catalyst Composite 11 and are given in Table II below.

20 Table II

Catalyst Composite	% zeolite in Catalyst	Nominal Zeolite SAR*	Mercury Intrusion Porosimetry Properties			Relative Deactivation Rate	
			Total PV* (ml/gram)	PV <300Å (ml/gram)	Macropore peak diameter, Å	Test 1	Test 2
1	80	60	0.461	0.140	1167	86	-
2**	80	60	0.436	0.156	931	61	46
4	80	60	0.449	0.149	1486	-	50

5	100	60	0.391	0.084	815	-	23
6	80	60	0.596	0.182	1664	67	-
7	65	6.7	0.488	0.270	1376	90	-
8	70	6.7	0.465	0.200	1591	100	-
9	80	60	0.575	0.174	1513	73	-
10	80	60	0.403	0.155	941	35	-
11	80	60	0.463	0.179	1110	43	-
12	80	60	0.399	0.144	900	-	35
13	80	60	0.449	0.163	1157	-	48
14	80	60	0.404	0.146	962	-	46
15	80	60	0.505	0.155	1738	-	100
16	80	60	0.444	0.162	1244	-	54
17	80	60	0.415	0.162	1031	-	46
18	80	60	0.421	0.136	1256	-	38

1

2 * Silica to alumina ratio in the crystalline zeolite powder.

3 ** Catalyst Composite 2 in Table II was prepared as the Catalyst Composite 2
4 in Table I, except that Catalyst Composite 2 in Table II contained more than
5 one batch of catalysts composites prepared in the manner of Catalyst
6 Composite 2 of Table I.

7 Effect of silica to alumina ratio on reduction in deactivation rate

8 Without being bound by any theory, it is believed that the higher silica to
9 alumina ratio and percent zeolite in the catalyst are important for obtaining
10 greater degree of reduction in relative deactivation rates with the catalyst
11 composites of this invention. In Table III, Catalysts 6 and 8 have similar
12 macropore peak diameters and cumulative pore volumes, but very different
13 silica to alumina ratios. By increasing the silica to alumina ratio from 6.7 to 60
14 and percent zeolite from 70 percent to 80 percent, the relative deactivation
15 rate of 100 of Catalyst 8 is reduced to 67 of Catalyst 6.

1

Table III

			Mercury Intrusion Porosimetry Properties			Relative Deactivation Rate
Catalyst Composite	% zeolite in Catalyst	Nominal Zeolite SAR*	Total PV* (ml/gram)	PV <300Å (ml/gram)	Macropore peak diameter, Å	Test 1
6	80	60	0.596	0.182	1664	67
8	70	6.7	0.465	0.200	1591	100

2

3

Effect of peak macropore diameter on reduction in deactivation rate

4 Without being bound by any theory, it is believed that the peak macropore
5 diameter has an effect on the deactivation rate of the catalyst composites of
6 this invention. A higher peak macropore diameter results in a higher relative
7 deactivation rate. In Table IV, Catalyst Composites 9 and 10 are compared
8 because, although they both differ slightly in the cumulative pore volume,
9 174 versus 155, Catalyst Composite 9 has a much higher peak macropore
10 diameter and a much higher relative deactivation rate, 1513 and 73,
11 compared to Catalyst Composites 10, 941, and 35.

12

Table IV

			Mercury Intrusion Porosimetry Properties			Relative Deactivation Rate
Catalyst Composite	% zeolite in Catalyst	Nominal Zeolite SAR*	Total PV* (ml/gram)	PV <300Å (ml/gram)	Macropore peak diameter, Å	Test 1
9	80	60	0.575	0.174	1513	73
10	80	60	0.403	0.155	941	35

13

1 Effect of cumulative pore volume on deactivation rate

2 Without being bound by any theory, it is believed that lowering the cumulative
 3 pore volume at pore diameters less than or equal to 300 angstroms results in
 4 lower deactivation rates. In Table V, Catalyst Composites 16 and 18 differ
 5 only by the cumulative pore volume, 162 and 136, respectively, and Catalyst
 6 Composite 16 has a higher relative deactivation rate, 54, compared to
 7 Catalyst Composites 18, 38.

8 Table V

Catalyst Composite	% zeolite in Catalyst	Nominal Zeolite SAR*	Mercury Intrusion Porosimetry Properties			Relative Deactivation Rate
			Total PV* (ml/gram)	PV <300Å (ml/gram)	Macropore peak diameter, Å	Test 2
16	80	60	0.444	0.162	1244	54
18	80	60	0.421	0.136	1256	38